

# Granitic groundwater colloids sampling and characterisation: the strategy for artefact elimination

A. C. Nilsson · I. Hedqvist · C. Degueldre

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**Abstract** Colloids were separated by submicro-filtration of granitic groundwater samples collected at-line under in-situ thermodynamic conditions after down-hole groundwater sampling and transfer at the well head. The methodology avoids the generation of artefacts produced by pH changes due to CO<sub>2</sub> exchange, yielding potential carbonate precipitation, or by O<sub>2</sub> contamination yielding oxidized insoluble phases. The enhanced pressure and the anoxic conditions are also maintained through the filtering procedure. This procedure was carried out after a period of regular sampling of groundwater pumped to the ground surface and continuous on-line long-term measurements (weeks, months) of chemical and physical parameters in the unbroken sample water both at the ground surface and at depth down-hole. Colloid samples were characterized on the submicro-filtration membrane by scanning electron microscopy. Under deep granite groundwater conditions, natural colloids occur sparsely. The colloid concentration was determined  $C_{\text{col}} \sim 1$  and  $\sim 50 \mu\text{g L}^{-1}$  for sizes ranging

from 50 to 200 nm or  $n_{\text{col}} \sim 3.9 \times 10^9$  and  $47 \times 10^9 \text{ L}^{-1}$  for sizes larger than 50 nm for KFM11A, Forsmark, and KLX17A, Laxemar, Oskarshamn, respectively, Sweden. These colloids are expected to be clay particles with an average size smaller than 200 nm for the Na-Ca-Cl and Na-Cl groundwaters (pH 7.6 and 8.00, ionic strength  $\sim 10^{-1}$  and  $\sim 10^{-2} \text{ mol L}^{-1}$ , respectively, for KFM11A and KLX17A), the colloid concentrations were comparable with values previously reported in the literature.

**Keywords** Aerosols/particulates · Electron/ion microprobe · Imaging (NMR microscopy/electron microscopy) · Nanoparticles/nanotechnology · Geochemistry/geology

## Introduction

Colloids are present in all ground waters [1]. Trace element properties in water may be affected by their association with colloids [2]. These colloids are defined as particles of size ranging from 1 to 1000 nm [3]. To evaluate the impact of contaminant transport by colloids, information on colloid concentrations, size distribution, and chemical nature is needed. Effective studies on groundwater colloids require careful collection and analysis of the groundwater prior to sampling [4] and characterisation [5] of the colloids. Colloid sampling and characterization procedures have been effectively reviewed [5] and it was clearly pointed out that sampling must be optimized in all cases prior to characterization. Today various techniques, including single-particle counting or colloid bulk analysis, are available involving on-site sampling and characterisation on-line or off-line. For example, samples can be taken on site and characterised directly at the site by light scattering. Or alternatively samples can be separated by filtration and

A. C. Nilsson  
Geosigma AB,  
Svärtdvagen 25B,  
18233 Dandery, Sweden

I. Hedqvist  
SKB Platsundersökningar,  
Simpevarp,  
572 95 Figeholm, Sweden

C. Degueldre (✉)  
Paul Scherrer Institute,  
5232 Villigen, Switzerland  
e-mail: claude.degueldre@psi.ch

C. Degueldre  
University of Geneva,  
1200 Geneva 4, Switzerland

filters can be sent for characterisation. In all cases artefact tracking is required, e.g. assessment of the enhancement of the amount of colloid by increasing the volume of the groundwater sample. However, this work requires resources that are not always available.

The colloid concentration of deep ground waters is usually around the  $\mu\text{g L}^{-1}$  level [5] and thus the contamination risks are obvious during water sampling and colloid sample preparation. Colloidal particles can be generated as artefacts, even proceeding to on-line sample preparation. The sampling errors are due to:

- excessively high or low pump rates,
- contamination from borehole activities,
- complex hydrological situations,
- contamination from tubes varying the composition of the groundwater,
- air contamination ( $\text{O}_2$  uptake),
- losses or uptake of  $\text{CO}_2$ ,
- aggregation-coagulation effects,
- long storage times prior to analyses,
- analytical errors, etc.

Some errors in the sampling and analysis of colloids are easy to avoid, others are difficult to evaluate.

The two sites, KFM11A, Forsmark, and KLX17A, Laxemar, Oskarshamn, for the present colloid study are located on the Scandinavian granite mole. At these locations the cooperative for the nuclear waste management in Sweden (SKB) is investigating a potential site for a deep repository for spent nuclear fuel. The site investigations involve, among other work, drilling of boreholes in order to study the geological, hydrogeological and hydrochemical conditions in the bedrock down to 1000 m depth. The host rock is in both cases metamorphosed granite where water-bearing fracture zones or single fractures occur relatively scarcely (Forsmark) or at a more normal frequency (Laxemar). Preliminary hydrogeochemical descriptions of the two sites have been reported [6, 7]. In these systems the water-bearing fractures also contain small amounts of clay minerals (e.g. chlorite, illites [8]).

This study presents and discusses the sampling and characterisation of granite groundwater colloids from KFM11A, Forsmark, and KLX17A, Laxemar, Oskarshamn, Sweden. Extensive hydrogeochemical studies of the system were performed prior to starting the colloid program.

## Experimental and methodology

### The hydrogeochemical system

Borehole KFM11A was drilled with a conventional rotary drilling system [9]. The 851.2 m long borehole was

completed at a vertical depth of 713.2 m in November 2006. The borehole intersects a major deformation zone starting at approximately 500 m borehole length. However, water for this study was pumped/sampled from a flow anomaly at 452.7 m borehole length (391.0 m vertical depth) in a fractured part of the bedrock adjacent to this zone. Prior to the investigation period, nitrogen flushing was performed several times from the bottom of the borehole and contemporaneous efficient pumping was maintained from the top of the borehole. In this way a water volume close to  $1000 \text{ m}^3$  was exchanged in order to reduce the content of remaining flushing water from drilling of the borehole. At the start of the investigation period in the sampling section, the drilling water content was still several percent. Due to the continuous pumping at a flow rate of about  $100 \text{ mL min}^{-1}$  for regular water sampling from the borehole section (447.5–454.6 m), this content was reduced to a few percent at the time of the in-situ water sampling for colloid filtration [10].

Borehole KLX17A was also drilled with a conventional rotary drilling system. The 701 m long borehole drilling was completed at a vertical depth of 607 m in 2006. Differential flow logging revealed several water-bearing fractures along the borehole. The borehole section at 416.0 to 437.5 m borehole length (333–352 m m.b.s.l.) was selected for investigation (including colloid study) due to a suitable hydraulic transmissivity and its location close to planned repository depth [11].

Down-hole equipment, consisting of from the top; umbilical hose, length mark detector, measurement cell for in-situ measurements, upper packer, borehole pump, in situ water sampler and lower packer, were installed in the boreholes and the borehole sections were isolated by the packers. Water samples were collected regularly at the ground surface during long pumping and measurement periods. Prior to lifting the equipment the valves to the in-situ sampling containers were opened from the surface in order to rinse the system and fill the containers. After some hours the valves were closed and the water sample portions for analyses of colloids, dissolved gases, and microbes were secured. Following stopping of the borehole pump and deflation of the packers, the equipment was lifted and the different down-hole units were dismantled.

Water samples were collected regularly at the ground surface during four and seven weeks pumping and measurement periods at Forsmark and Laxemar, respectively. The flow rate was approximately  $100 \text{ mL min}^{-1}$  in both cases. Following stopping of the borehole pump and deflation of the packers, the equipment was lifted and the down-holes units were dismantled. The remaining flushing water contents from borehole drilling were close to 6% (KFM11A) and 2% (KLX17A) at the time of the in-situ water sampling for colloid filtration.

## Water sampling and analysis

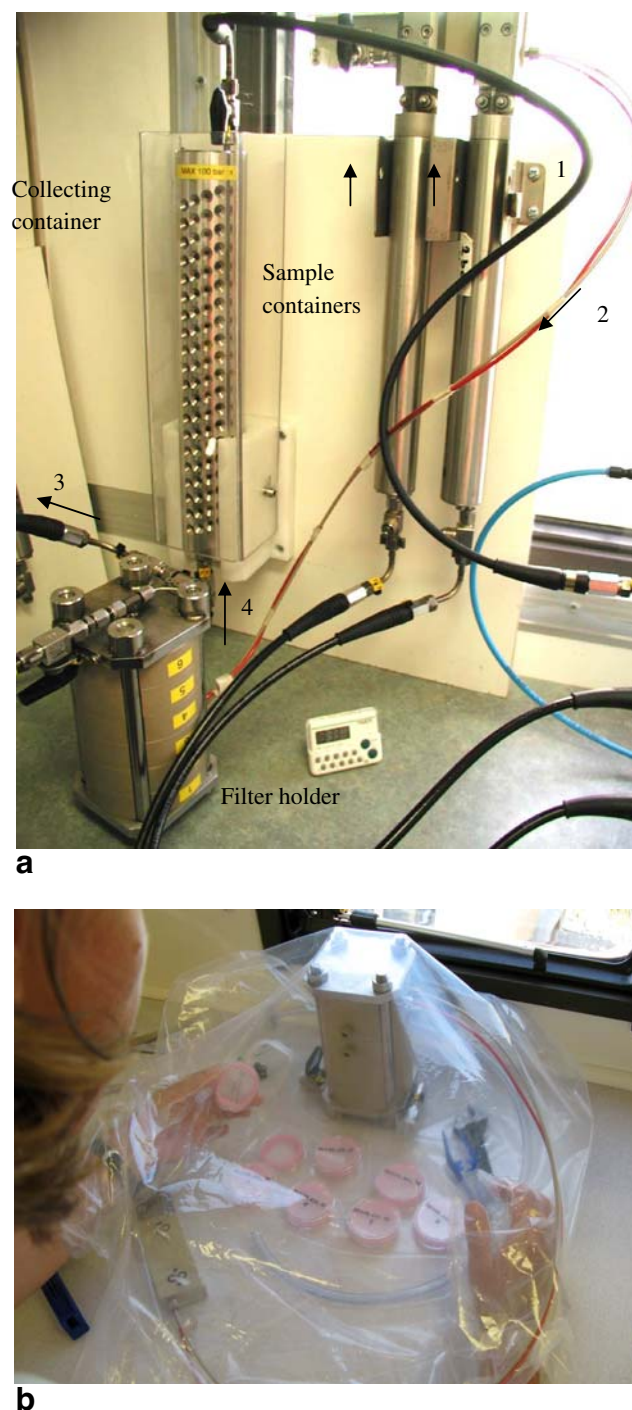
Regular water sampling was performed from pumped water, and filtration of sample portions for chemical analyses was performed by connecting the filter holders directly to the outlet tubing made of polyamide. Field pH was measured on-line in the unbroken water line with glass and Ag/AgCl reference electrodes in measurement cells down-hole in the borehole section and at the ground surface. Laboratory pH was measured in batch samples at 25 °C using a combined electrode. The pH was measured to  $\pm 0.02$  units after careful standardisation with buffers (4, 7, and 10). *Eh* was measured by Au, Ag, and Pt electrodes against Ag/AgCl reference electrodes in the same flow-through cells (at the surface and in the borehole section) as the pH measurements.

Analyses of Fe(II), alkalinity, ammonium, laboratory pH, and electrical conductivity were performed immediately after each sampling at the site. The other analyses were performed by several consulted laboratories and the water was analysed for its dissolved and suspended solid contents. Mohr titration (chloride) and ion chromatography (Dionex 120) were utilised for assaying major anions. Total organic carbon (TOC) and dissolved organic carbon (DOC) were determined using a Shimadzu TOC-5000 carbon analyser. ICP–AES and ICP–MS techniques were used for minor and minor elements.

## Colloid analysis methodology

The in-situ groundwater samples were lifted to the ground surface at maintained pressure from the borehole section. Selected samples were used to obtain colloid samples on filters. The entire filtration procedure was performed under argon atmosphere and at maintained pressure from the borehole section. The colloid filtering system allowed submicro filtration of groundwaters through five connected filters in a closed system under argon atmosphere (Fig. 1a). The filtering was performed at a pressure similar to that of the groundwater in the borehole section and five filters in the pore-size order 2, 2, 0.4, 0.2, and 0.05  $\mu\text{m}$  were used. The two first filters were used to prevent clogging. The membranes of diameter 47 mm are mounted with a 1.8-mm O-ring and the volume of water,  $V_f$ , was 140 mL. The system was maintained at 9.8 and 14 °C (KFM11A and KLX17A respectively) under isothermal and isobaric (MPa) conditions and maintained under the in-situ conditions for filtration. Filtration was carried out with a differential pressure of 0.3 MPa, it was followed by a rinsing phase with a small volume (10 mL) of de-oxygenated, de-ionised water through the five connected filters. This procedure allows washing of the membrane and avoids salt precipitation in the last step when drying the

colloid cake. The filters were subsequently dried, handled in portable glove box as depicted Fig. 1b and stored under argon in Petri dishes in welded plastic bags in a fridge prior to transfer in the laboratory.



**Fig. 1** **a.** Overview of the sampling container and of the filtration cell, the arrows (1–4) show the flow direction of the water through the system; **b.** View during the filter packing in the portable glove box. The filters are set in the unit and used under pressure during the filtering. The sampling time was performed in 16 minutes, a last membrane washing is carried out with small aliquot of ultra-pure water



The 0.2 and 0.05- $\mu\text{m}$  pore-size membranes were investigated by scanning electron microscopy (SEM). Particle analysis was carried out by energy-dispersive spectroscopy (EDS). The SEM investigations were performed with a Zeiss DSM 962 unit under 30 kV. SEM investigations had previously been tested with gold colloids as recently reported by Degueldre et al. [12]. For the current tests the filter membranes were coated with a 15-nm Pt layer by magnetron sputtering prior to microscopic investigations. The energy-dispersive spectroscopic (EDS) analysis was performed using the Zeiss unit. This single-particle monitoring allows specific counting of three size classes from 50 to 100, 100 to 150, and 150 to 200 nm.

### Colloid analysis methodology

The number of colloid particles,  $n$ , detected on a micrograph (surface  $s$ ) of the membrane of surface  $S$  may be translated into the number of particles,  $N_{\text{col}}$ , in a volume of filtered water  $V$ . The colloid number concentration  $N_{\text{col}}$  is simply given by:

$$N_{\text{col}} = \frac{n \cdot s}{V \cdot S} \quad (1)$$

The colloid number concentration  $N_{\text{col}}$  may be modelled as a function of their size  $d$  using a power law size distribution:

$$\frac{\Delta N_{\text{col}}}{\Delta d} = A \cdot d^{-b} \quad (2)$$

where  $A$  and  $b$  are constant for given size ranges. The colloid mass concentration  $C_{\text{col}}$  may be calculated assuming spherical colloids of density  $\rho$ :

$$\frac{\Delta C_{\text{col}}}{\Delta d} = \frac{\pi \cdot A \cdot \rho}{6} \cdot d^{3-b} \quad (3)$$

Concentrations were calculated for the size range  $d_{\text{min}} - d_{\text{max}}$  by integrating the colloid number concentration over the size interval. Calculations were originally done by using the COLIAT code based on particle size distribution including shape hypothesis [3], however, the number of colloids was not large enough to present aggregates, and, simple calculation was carried out size-class-wise.

## Results and discussion

### Ground water colloid characterisation

The KFM11A groundwater is of a Na-Ca-Cl type, with an  $Eh$  of  $-0.203 \pm 0.013$  mV and a pH of  $7.6 \pm 0.1$ . The KLX17A groundwater is of a Na-Cl type, with an  $Eh$  of  $-0.297 \pm 0.013$  mV and a pH of  $8.0 \pm 0.1$ . The granitic water chemistries are given in Table 1.

**Table 1** Element concentrations in the studied granitic groundwaters. KFM11A:(F) pH  $7.58 \pm 0.10$ ,  $T$   $9.8$  °C, TOC 1.1 ppm,  $Eh$   $-0.203 \pm 0.013$  V. KLX17A:(L) pH  $8.00 \pm 0.10$ ,  $T$   $12$  °C, TOC 3.3 ppm,  $Eh$   $-0.297 \pm 0.010$  V

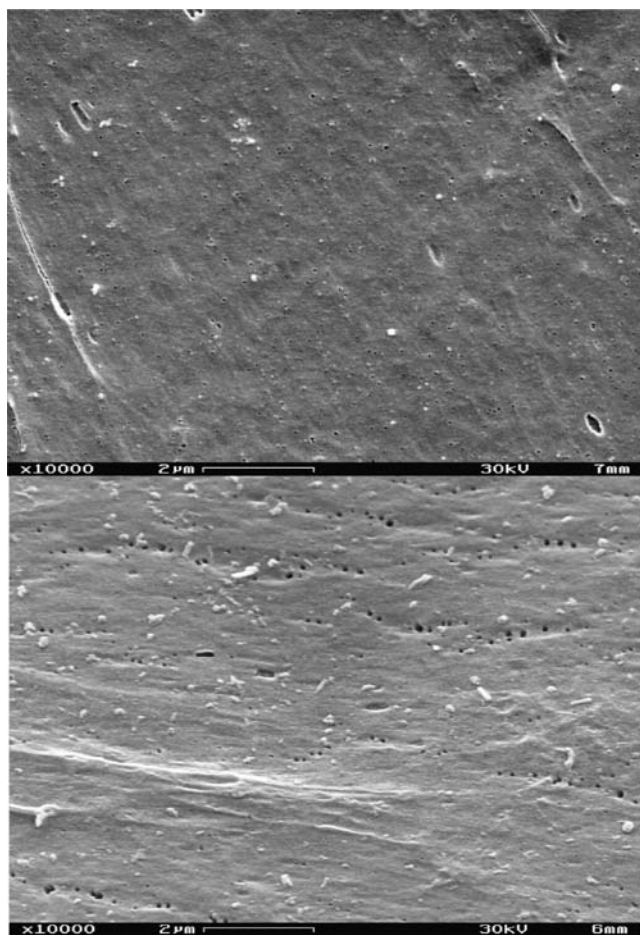
Element	C(F)/M	C(L)/M
Al	$1.008 \times 10^{-6}$	$1.607 \times 10^{-7}$
Br	$2.092 \times 10^{-4}$	$2.757 \times 10^{-5}$
C (HCO <sub>3</sub> )	$3.944 \times 10^{-4}$	$1.887 \times 10^{-3}$
Ca	$3.216 \times 10^{-2}$	$1.729 \times 10^{-3}$
Cl	$1.196 \times 10^{-1}$	$1.669 \times 10^{-2}$
Fe	$4.327 \times 10^{-6}$	$1.362 \times 10^{-6}$
K	$1.527 \times 10^{-4}$	$4.016 \times 10^{-4}$
Li	$6.821 \times 10^{-6}$	$7.834 \times 10^{-6}$
Mg	$1.553 \times 10^{-3}$	$1.027 \times 10^{-4}$
Mn	$2.255 \times 10^{-6}$	$1.968 \times 10^{-5}$
Na	$5.475 \times 10^{-2}$	$1.442 \times 10^{-2}$
S (SO <sub>4</sub> )	$9.958 \times 10^{-4}$	$2.543 \times 10^{-4}$
Si	$9.989 \times 10^{-5}$	$1.391 \times 10^{-4}$
Sr	$1.965 \times 10^{-4}$	$1.965 \times 10^{-5}$

Analysis of the colloids by scanning electron microscopy on the prepared membranes revealed colloids of various sizes, shapes and morphologies, as can be seen Fig. 2a,b. The micrographs taken for ground water colloid samples on a 0.2  $\mu\text{m}$  membrane are not presented. The 0.2–0.3  $\mu\text{m}$  colloid number  $n$  on the membrane is very low. Occasionally a larger particle is found in all the 10 to 30 micrograph fields of magnification 10,000. These particles should be seen as artefacts in the aquifer because they should settle in situ. The observed 200 nm colloids are likely to be generated during the sampling. They are too small to be identified by EDS.

Figure 2a,b show typical micrographs taken for KFM11A and KLX17A ground water colloid samples on 0.05  $\mu\text{m}$  membranes. The colloid number  $n$  on the membrane is significant. It must be noted that these colloids attach to the membrane and do not clog pores. Some pores seem to be apparently larger than 0.05  $\mu\text{m}$ , however, their structures below the membrane surface respect the cut off. The examined surfaces are covered with colloids and their density is sufficiently large on the active surfaces to calculate their concentration with a reasonable precision. On membrane KLX17A some small bacteria ( $\sim 200$  nm) are also identified in the micrographs.

Counting of the colloids was carried out systematically and the colloid concentrations were estimated using Eqs. 1–3. Table 2 gives details of the colloid concentration for the investigated sizes. The colloid size distributions are shown in Fig. 3.

Based on SEM micrographs, colloid morphology indicates the occurrence of particles with sizes smaller than 200 nm that are presumed to be clay particles because the filling material of the fissures are composed of clay



**Fig. 2** SEM micrographs of the ground water colloids (KFM11A up & KLX17A down)

minerals. Neither aluminium nor silicon is detectable by EDS, the colloid size being too small to allow analysis. X-ray diffraction XRD analysis of colloids from 0.10–1.00  $\mu\text{m}$  collected on membrane filters should be attempted, to analyse their clay nature; this requires filtration of water volumes at least 20 times larger which is not possible with the present instrumentation. These particles are expected from the rock mineralogy described in the Experimental section. The colloid concentrations  $C_{\text{col}}$  in the granitic ground waters investigated are  $\sim 1$  and  $\sim 40 \mu\text{g L}^{-1}$  respectively for KFM11A and KLX17A, for the 50–200 nm size range and for a colloid density of  $2 \text{ g cm}^{-3}$ .

### Assessing the colloid data

In order to assess the quality of the colloid data, it is imperative to understand if the water quality is affected or not by the borehole construction and packer installation [13]. In principle the artefacts from bore hole construction and packer installation have been purged out and discarded by dilution during the week flush out. Submicro-filtration of the colloids is carried out after on-line long-term measurements (weeks, months) of chemical and physical

parameters in the unbroken sample water line both at the surface and at depth down-hole.

In situ, colloid transit during pumping in the borehole line creates a cut-off (balance between transport upward and sedimentation). A particle of size  $d$  acquires, in the bore hole, a constant settling velocity  $v$  given by Stoke's law:  $v = 0.05556gd^2(\rho - \rho_w)\eta^{-1}$ , where  $g$  is the acceleration due to gravity ( $981 \text{ cm s}^{-2}$ ),  $\rho_w$  the water density, and  $\eta$  the fluid viscosity ( $1.4 \text{ cPoise}$  or  $1.4 \times 10^{-3} \text{ Pa s}$  at  $10^\circ\text{C}$ ). A colloid density of  $2 \text{ g cm}^{-3}$  corresponds to the maximum size for which transit from the interval to the container may be determined. Large colloids may concentrate in the interval while small are extracted. However, large particles are filtered off by the two first membranes, each of  $2\text{-}\mu\text{m}$  cut off.

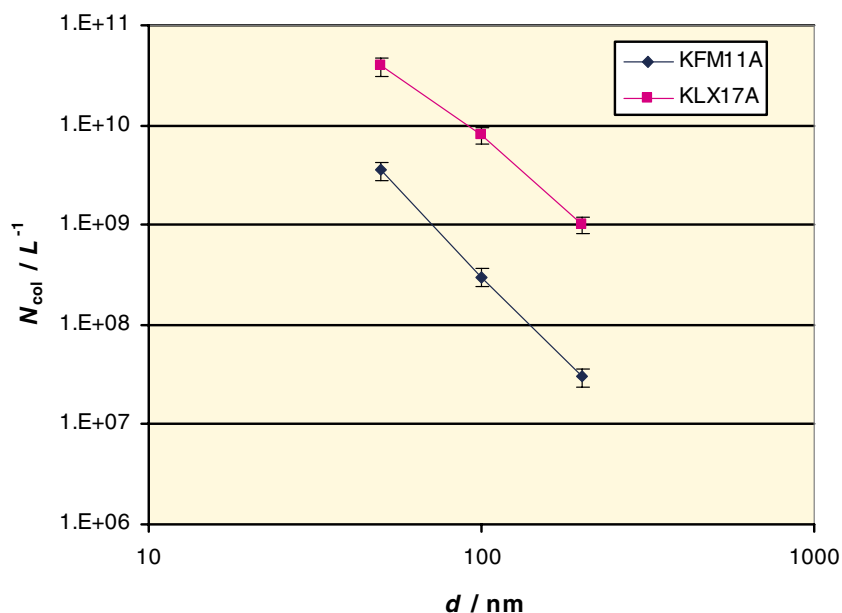
Residence time in the interval from the water-bearing zone to the container aperture is also important. During this period, the aggregation of the colloids in the size range considered should not be significant (the aggregation half-time has to be estimated for a colloid concentration of 1 ppm or 1 ppb and for attachment coefficients of the order of  $10^{-1}$  to  $10^{-3}$  (corresponding to the Ca, Mg, Na, and K concentration) and size 100 nm [14].

From the chemistry point of view the question is: are colloids affected by the presence of precipitated phases? The generation of artefacts produced by pH changes due to  $\text{CO}_2$  exchange, yielding potential carbonate precipitation, or by  $\text{O}_2$  contaminations yielding oxidised insoluble phases was evaluated by running the PHREEQ model [15] for the data reported in Table 1 for both in-situ and filtration temperatures. The results are given in Table 3 and show that the saturation indices are similar in situ and during filtration. For pH 8.0 and 7.6 and for the concentrations of bicarbonate, calculations show that the carbonates of Ca, Mg, Sr, Fe, and Mn are undersaturated (or near saturation, e.g. calcite) and that the partial pressure of  $\text{CO}_2$  is  $10^{-3.14}$  and  $10^{-3.40}$  Atm. The water could release a small amount of its  $\text{CO}_2$ , slightly increasing its pH; the filtration is carried out with a slight overpressure, however, making calcite precipitation unlikely. The oxy-hydroxides are undersaturated or very slightly saturated, e.g. Al, Fe, Mn, Si. Finally the clay minerals are slightly oversaturated. The on-line procedure allows working at the well head at  $T$  and  $P$

**Table 2** Comparison of KFM11A and KLX17A groundwater colloid data

$d$ (nm)	KFM11A		KLX17A	
	$N_{\text{col}}$ ( $\text{L}^{-1}$ )	$C_{\text{col}}$ ( $\text{mg L}^{-1}$ )	$N_{\text{col}}$ ( $\text{L}^{-1}$ )	$C_{\text{col}}$ ( $\text{mg L}^{-1}$ )
50	$36 \times 10^8$	0.00014	$39 \times 10^9$	0.016
100	$3 \times 10^8$	0.0009	$8 \times 10^9$	0.024
>200	$(0.3) \times 10^8$	0.0008	$(1) \times 10^9$	0.056
50–200	$39 \times 10^8$	$\sim 0.001$	$47 \times 10^9$	$\sim 0.040$

**Fig. 3** Colloid size distributions estimated from data reported in Table 2. Conditions: error bares 20%



**Table 3** PHREEQ indicative results obtained for the water chemistries given in Table 1. Conditions: KFM: Electr. Bal.= $5.830 \times 10^{-4}$  eq, at 9.8 °C, It.=7; KLX: Electr. Bal.= $2.516 \times 10^{-4}$  eq, at 12 °C, It.=11;  $KT$  values at 9.8 °C

Phase	$SI(F)$	$SI(L)$	$\log KT$
Alumina(a)	-1.16	-2.46	11.84
Albite	-0.43	-1.46	5.32
Alunite	-2.50	-12.94	0.58
Anhydrite	-1.34	-4.81	-4.34
Anorthite	-1.99	-4.33	28.51
Aragonite	-0.26	-8.51	-8.25
Calcite	-0.10	0.07	-8.41
Celestite	-1.25	-4.46	-6.63
Chalcedony	-0.25	-0.15	-3.74
Chlorite(14A)	-5.85	-4.70	74.35
Chrysotile	-6.71	-4.48	34.18
CO <sub>2</sub> (g)	-3.40	-3.14	-18.22
Dolomite	-1.60	-0.54	-16.72
Gibbsite	1.68	0.36	9.01
Gypsum	-1.08	-4.55	-4.59
Hausmannite	-29.89	-28.24	64.99
Illite	2.18	-0.12	13.56
K-feldspar	-0.24	-0.88	2.55
Kaolinite	4.58	2.12	8.82
Pyrochroite	-6.31	-5.26	15.20
Pyrolusite	-26.61	-27.29	43.94
Quartz	0.23	0.32	-4.22
Rhodochrosite	-1.66	-0.32	-11.07
Sepiolite	-4.51	-2.95	16.18
Siderite	-1.61	-0.88	-10.79
Silica(a)	-1.14	-1.03	-2.84
Strontianite	-1.43	-1.00	-9.29

conditions similar to the in-situ conditions, i.e. artefact free. This methodology avoids the generation of artefacts produced by pH changes due to CO<sub>2</sub> exchange, yielding potential carbonate precipitation, or by O<sub>2</sub> contamination, yielding oxidised insoluble phases. The at-line, at well head, procedure allows artefact-free working.

The colloid concentrations were determined  $C_{col} \sim 1$  and  $40 \mu\text{g L}^{-1}$  for sizes ranging from 50 to 200 nm or  $N_{col} \sim 3.9 \times 10^9$  and  $47 \times 10^9 \text{ L}^{-1}$  for sizes larger than 50 nm for KFM11A and KLX17A, respectively. These colloids are suggested to be clay-like. The particle concentrations are indicative since they concern single filtration campaigns. The results are, however, consistent with the colloid data for granitic ground water systems. These concentration values are comparable with those obtained so far for the Swiss granitic groundwaters as summarised in Table 4 [3].

In the granitic groundwater at Grimsel, Leuggern, and Zurzach, Switzerland, where the concentration of Na is around  $10^{-3}$  to  $10^{-2} \text{ mol L}^{-1}$  and TOC low (<1 ppm) the colloid concentration is approximately 20 ppb for sizes ranging from 50 to 200 nm [3]. In KFM11 the concentration of divalent cations (Ca(II), Mg(II), Fe(II)) is  $4 \times$

**Table 4** Comparison of KFM11A and KLX17A groundwater colloid data with the Swiss data [3]. Conditions:  $d$  50–200 nm

	KFM11A	KLX17A	Leuggern	Grimsel
pH	7.5	8.0	8.0	9.6
$I$ (eq)	$\sim 10^{-1}$	$\sim 10^{-2}$	$\sim 10^{-2}$	$\sim 10^{-3}$
TOC(ppm)	1.1	3.3	0.03	0.03
$C_{col}$ (ppb)	$\sim 1$	$\sim 40$	$\sim 20$	$\sim 20$

$10^{-2}$  mol L<sup>-1</sup>, which is able to enhance colloid attachment (attachment coefficient  $10^{-2}$  to  $10^{-1}$ ), which contributes to colloid attachment and aggregation. However, TOC is >1 ppm, favouring colloid stability. In the KFM11A groundwater the colloid concentration is somewhat lower than in KLX17A groundwater because of the larger ionic strength in the water destabilising the colloid population. In deep granitic groundwater conditions, natural colloids occur. The colloid concentration was determined to be  $C_{\text{col}} \sim 1\text{--}40$   $\mu\text{g L}^{-1}$  for sizes ranging from 50 to 200 nm for KFM11A and KLX17A. These colloids are expected to be clay particles with an average size smaller than 200 nm. For the Na-Ca-Cl and Na-Cl groundwaters (pH 7.53 and 8.00, ionic strength  $\sim 10^{-1}\text{--}10^{-2}$  mol L<sup>-1</sup>, respectively for KFM and KLX), the colloid concentrations are comparable with values reported earlier.

## Conclusions

Samples of natural ground water colloids were produced by submicro filtration at-line, at the well head, from granitic ground waters under in-situ *T* and *P* conditions. This methodology avoids the generation of artefacts produced by pH changes due to CO<sub>2</sub> exchange, yielding potential carbonate particles, or by O<sub>2</sub> contamination, yielding oxyhydroxide colloids. The at-line procedure enables artefact free working at the well head. Submicro-filtration of the colloids is carried out after on-line long-term measurements (weeks, months) of chemical and physical parameters in the unbroken sample water line both at the surface and at depth down-hole. Colloid samples were characterised by scanning electron microscopy. In the deep granitic groundwater conditions, natural colloids occur. The colloid concentrations were determined to be  $C_{\text{col}} \sim 1$  and  $40$   $\mu\text{g L}^{-1}$  for sizes ranging from 50 to 200 nm or  $N_{\text{col}} \sim 3.9 \times 10^9$  and  $47 \times 10^9$  L<sup>-1</sup> for sizes larger than 50 nm for KFM11A, Forsmark, and KLX17A, Laxemar, Oskarshamn, respectively, Sweden. These colloids are suggested to be clay particles with an average size smaller than 200 nm. For the Na-Ca-Cl and Na-Cl groundwaters (pH 7.5 and 8.00, ionic strength  $\sim 10^{-1}$  and  $\sim 10^{-2}$  mol L<sup>-1</sup>, respectively, for KFM11A and KLX17A), the colloid concentration values are comparable with values previously reported in the literature.

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